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Inventor(s): Becker et al.

**METHOD FOR ENHANCING OXIDE TO NITRIDE SELECTIVITY
THROUGH THE USE OF INDEPENDENT HEAT CONTROL**

Cross-Reference to Related Applications

- IN 1/*
~~This is a continuation application of co-pending U.S.~~
5 Application Serial Number 08/905,891, filed August 4, 1997; which was a continuation of U.S. Application Serial Number 08/152,755, filed November 15, 1993, which issued as U.S. Patent Number 5,880,036 on March 9, 1999; which was a continuation-in-part of application Serial Number 07/898,505, filed June 15, 1992, which 10 issued as U.S. Patent Number 5,286,344 on February 15, 1994..

Field of the Invention

This invention relates to semiconductor manufacturing, and more particularly to a process for selectively etching a silicon dioxide layer disposed on a silicon nitride layer, useful when etching features have submicron geometries.

Background of the Invention

With geometries shrinking, it is becoming more difficult to align small contacts in between closely spaced wordlines or other conductive structures. Therefore, an etch is needed which would 20 etch an oxide layer and stop on the underlying nitride layer. The highly selective etch should also display consistency for manufacturing purposes.

Current manufacturing processes of multilayer structures typically involve patterned etching of areas of the semiconductor 25 surface which are not covered by a pattern of protective photoresist material. These etching techniques use

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liquid or wet etching materials, or dry etching with halogens or halogen-containing compounds.

Etching of the multilayer structures can also be conducted in a gas phase using known techniques, such as plasma etching, ion beam etching, and reactive ion etching. The use of gas plasma technology provides substantially anisotropic etching using gaseous ions, typically generated by a radio frequency (RF) discharge.

In gas plasma etching the requisite portion of the surface to be etched is removed by a chemical reaction between the gaseous ions and the subject surface. In the anisotropic process, etching takes place primarily in the vertical direction so that feature widths substantially match the photoresist pattern widths. Anisotropic etching is utilized when feature sizing after etching must be maintained within specific limits so as not to violate alignment tolerances or design rules.

Higher density multilayer structures such as 64 and 256 Megabit DRAM require an additional amount of alignment tolerance which can not be addressed by current photolithographic means. In such applications, an etch stop technology could be used to supply the desired tolerance.

In an etch "stop" system, an etch "stop" layer is deposited on underlying structures. The superjacent layer is disposed over the underlying etch "stop" layer through which the desired patterns will be defined. The etch "stop" layer will then be used to terminate the etch process once the superjacent layer has been completely removed in the desired pattern locations. Thus, the etch "stop" layer acts to

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protect structures underlying the etch "stop" layer from damage due to the dry chemical etch of the superjacent layer.

5 The preferred etch "stop" material is silicon nitride because its properties are well known, and it is currently used for semiconductor fabrication. The preferred superjacent layer is silicon dioxide, or other oxide such as, BPSG.

10 The etch stop process must have three basic properties, namely, (1) a high etch rate for the superjacent layer which (2) produces substantially vertical sidewalls, and (3) has a high selectivity of the superjacent layer being etched down to the etch "stop" layer.

15 A problem of profile control occurs with respect to etching of a multilayer structure having a silicon dioxide layer disposed on an underlying silicon nitride layer. Profile control using pure chemical etching (e.g., using hydrofluoric acid) tends to produce structures that do not have vertical sidewalls.

20 Dry etch processing usually produces a more vertical profile because of the ion bombardment aspect of the process. However, the dry etch process can produce a contact wall that slopes out from the bottom, rather than at an angle of 90°, if the wrong mix of process parameters are used. These parameters can include, but are not limited to; fluorocarbon, RF power, and pressure.

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The same ion bombardment aspect of the dry etch process used to produce straight sidewalls has a very negative effect on oxide to nitride selectivity. High energy ions needed to etch both oxide and nitride do so by disassociating a chemical bond at the oxide and/or nitride surface. However, the disassociation energy needed for nitride is less than that required for oxide.

Hence, CH_2F_2 is added to offset the disassociation properties of nitride as compared to oxide. The CH_2F_2 produces a polymer deposition on the nitride surface that acts to passivate the nitride surface and thereby reduce the dry etch removal rate. However, the silicon dioxide etch rate is sustained at a much higher rate than that of silicon nitride.

Current etch process technology for etching an SiO_2 layer on an underlying Si_3N_4 layer using a dry etcher, such as an RIE or MRIE etcher, cannot produce SiO_2 -to- Si_3N_4 selectivities above 5-6:1 with adequate profile and SiO_2 etch rate characteristics.

Almost all of the current etch processes which involve high selective etches, rely on cooler temperatures to obtain those selectivities. See, for example, "Temperature Dependence of Silicon Nitride Etching by Atomic Fluorine," and "Selective Etching of Silicon Nitride Using Remote Plasmas of CF_4 and SF_6 ," both by Lee M. Loewenstein. The latter reference uses an Arrhenius plot having a negative slope to illustrate that the nitride etch rate increases as a function of substrate temperature.

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Therefore, a need exists for a process of etching a SiO_2 layer on an underlying Si_3N_4 layer, at a high SiO_2 etch rate. Furthermore, there exists a need for an etch at a high selectivity of SiO_2 with respect to the underlying Si_3N_4 , to form an etched multilayer structure at a controlled predetermined profile in which the resulting sidewalls are substantially normal to the substrate.

Summary of the Invention

- The present invention provides unexpected and very key improvements over the current etch processes. The present invention teaches away from current thought, by using increased temperatures to achieve increased selectivity. In addition to improved selectivity, the higher temperatures help reduce the polymer build-up inside the chamber.
- The process of the present invention meets the above-described existing needs by forming an etched multilayer structure, in which the sidewalls of the SiO_2 layer are substantially normal to the substrate, at a high SiO_2 etch rate, and at a high selectivity of SiO_2 with respect to the underlying Si_3N_4 . This is accomplished by heating various portions of the etch chamber while employing a process for etching the SiO_2 layer down to the Si_3N_4 stop layer.

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Brief Description of the Drawings

The present invention will be better understood from reading the following description of nonlimitative embodiments, with reference to the attached drawings, wherein below:

- 5 Figure 1 is a schematic cross-section of a multilayer structure having a silicon dioxide layer disposed on a silicon nitride "etch" stop layer, prior to etching with the fluorinated chemical etchant system of the present invention;
- 10 Figure 2 is a schematic cross-section of the multilayer structure of Figure 1, after the etch step according to the process of the present invention;
- 15 Figure 3 is a plot of oxide:nitride selectivity in relation to both the silicon anode temperature and the addition of CH_2F_2 ; and
- 20 Figures 4a-4c are Arrhenius plots illustrating the unexpected results obtained with the process of the present invention.

Detailed Description of a Preferred Embodiment

- 20 The inventive process herein is directed towards anisotropically etching a multilayer structure comprising a silicon dioxide outer layer on an underlying silicon nitride "stop" layer.

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Referring to Figure 1, a multilayer structure, which is formed by conventional techniques, is depicted. It will serve as a representative example. The multilayer structure of Figure 1, generally designated as 10, is shown prior to etching.

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The multilayer structure 10 comprises a plurality of structural layers which are sequentially disposed on an underlying silicon structure or wafer 18. Multilayer structure 10 comprises a plurality of structural layers including a layer 14 having a major outer surface 14a. Structural layer 14 is fabricated of SiO_2 .

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Generally, an undoped oxide 15, referred to as a field oxide or gate oxide, is usually grown in a furnace. Doped oxide includes BPSG, PSG, etc. which are generally deposited on the silicon wafer with a dopant gas(es) during a deposition process.

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The outer structural layer 14 is deposited onto an adjacent intermediate structural layer 16. Layer 16 includes sidewalls and is fabricated of an etch "stop" layer of silicon nitride.

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Also shown in Figure 1, is a chemical etchant protective patterned layer 12 which comprises a photoresist layer having a predetermined arrangement of openings 12a for forming a predetermined pattern in multilayer structure 10. Typically, this is accomplished using a semiconductor photomask, and known conventional etch mask patterning techniques.

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The etch "stop" layer 16 is disposed on the field oxide 15, silicon substrate 18, and onto a plurality of polysilicon lines 17 located adjacent to their respective sidewalls spacer elements 19.

5 As seen in Figure 2, the preferred manner of etching of the structural SiO_2 layer 14 down to etch "stop" layer 16 is by plasma etch. The gas plasma etch technique employed herein typically has an etching area in a plasma and is generated under vacuum within the confines of an RF discharge unit.

10 The preferred plasma etch technique employed herein may include the use of ECR (Electron Cyclotron Resonance), RIE, MIE, MERIE, PE reactive ion, point plasma etching, magnetically confined helicon and helical resonator, PE, or magnetron PE. In plasma dry etchers, typically the upper electrode is powered while the lower electrode is grounded.

15 In RIE (Reactive Ion Etchers), the lower electrode is powered while the upper electrode is grounded. In triode dry etchers, the upper and lower electrodes can be powered as well as the sidewall. In MERIE (magnetically enhanced reactive ion etch) magnets are used to increase the ion density of the plasma. In ECR (Electron Cyclotron Resonance), the plasma is generated upstream from the main reaction chamber. This produces a low ion energy to reduce damage to the wafer.

20 A semiconductor device is disposed in the desired etcher, within an etching area, and is etched with a fluorinated chemical etchant system to form a predetermined pattern therein. The fluorinated chemical etchant system comprises a chemical etchant composition, such as, for example, $\text{CHF}_3\text{-CF}_4\text{-Ar}$, and a CH_2F_2 additive material. The fluorinated chemical

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etchant system is in a substantially gas phase during the etching of the multilayer structure 10.

5 The exposed SiO_2 layer 14 is selectively etched at a relatively high etch rate down to the Si_3N_4 etch "stop" layer 16 by removing predetermined portions of the SiO_2 layer 14 by chemically enhanced ionic bombardment. Some areas of the wafer still had SiO_2 available for etching, while other areas of the wafer had already reached the nitride layer 16 where the etching process effectively stops because of polymer formation on the nitride surface. In this way, the etching process can provide for the formation of sidewalls in etched layers which have a substantially vertical profile.

10 The etching system employed in developing the process of this invention was the Applied Materials Precision 5000, a single wafer plasma etching apparatus manufactured by Applied Materials of Santa Clara, California. This apparatus comprises a mobile, double cassette platform, a transport chamber with an 8-wafer storage elevator, and from 1-4 plasma etching chambers.

15 The mobile cassette platform is maintained at atmospheric pressure during the entire operation of the apparatus. It holds two cassettes of wafers, each capable of holding up to 25 wafers. The platform can be raised or lowered and moved laterally so that any particular wafer may be aligned with a narrow door located between the platform and the transport chamber.

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- 5 Nitrogen gas is fed through a flow control valve into the transport chamber to vent the chamber to atmosphere. A robot transfer arm in the transport chamber transfers wafers from the cassette on the mobile cassette platform to the storage elevator in the transport chamber.

10 The transport chamber is connected to a two stage evacuation pump which is used to evacuate the transport chamber and maintain it at a suitable pressure for transporting wafers from the elevator to the plasma etching chamber. This pressure was maintained at 75-125 mTorr.

15 The plasma etching chamber is connected to a turbo pump and the two stage pump which evacuates the chamber to a lower pressure than that of the transport chamber. This pressure is typically less than 10 mTorr.

20 When the transport chamber and the plasma etching chamber have reached suitable pressures for wafer transfer, the robot arm transfers a wafer from the wafer storage elevator to the plasma etch chamber.

25 The plasma etching chamber contains an upper, electrically grounded electrode which also serves as the chamber sidewalls, and a lower, RF powered electrode upon which the wafer is clamped during the plasma etch process, and a set of electromagnetic coils placed around the chamber sidewalls.

30 In one embodiment of the present invention, an etch chamber having an upper electrode (or anode) which is comprised of silicon is used. It is believed that the silicon scavenges the free fluorine from the reaction, and thereby

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substantially prevents the free fluorine from etching the nitride layer 16.

In the process of the present invention, it has been unexpectedly found that an enhanced selectivity effect results with the addition of CH_2F_2 while using a hot silicon plate (or anode). For CH_2F_2 flows above 8 sccm, and silicon plate temperatures above 75°C, a significant result occurs, as depicted in plot of Figure 3. At a silicon plate temperature of 225°C, the selectivity of oxide:nitride increases from 1.7:1 without CH_2F_2 , to over 33:1 with the addition of 10 sccm CH_2F_2 .

The chamber also contains a gas distribution plate connected to the lid of the chamber, through which suitable feed gas mixtures are fed into the chamber from a connected gas supply manifold.

When RF energy is applied to the lower electrode, the gas fed into the chamber, via the gas distribution plate, is converted to plasma. The plasma contains reactive chemical species which etch selected unmasked portions of the wafer, which wafer is clamped to the lower electrode.

Electric power is applied to the electromagnetic coils which surround the chamber sidewalls. The magnetic field generated by the coils increases the density of the plasma near the wafer surface. A throttle valve located between the plasma etching chamber regulates the pressure of the chamber to processing values, generally in the range of 10-350 mTorr.

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The lower electrode is connected to a wafer cooling system designed to maintain the wafer at a constant temperature during the plasma etch process. This system consists of two parts. The first is an apparatus providing a temperature controlled fluid which circulates through a tunnel in the lower electrode.

The second part is an apparatus providing a pressure and flow controlled inert gas (typically helium) of high thermal conductivity which is fed to the underside of wafer during etch via a channel through the lower electrode, opening to grooves on the top face of the lower electrode. The helium gas is contained behind the wafer by an O-ring seal which lies partially in a circular groove in the lower electrode.

The second part is referred to as a helium backside cooling system. During plasma etches, power is dissipated in the plasma through the ionization of the gaseous species. During the ionization process, a large amount of heat is generated. The helium backside cooling system allows the heat which has been imparted to the wafer, to be more effectively coupled to the temperature controlled lower electrode. As the pressure in the helium cooling system is increased, the wafer temperature more closely matches the temperature of the lower electrode throughout the plasma process. Hence, a more stable and predictable process is possible.

When the clamp is lowered to clamp the wafer against the lower electrode, the wafer underside is held tightly against the O-ring seal. The seal prohibits leakage of the inert gas from underneath the wafer to the plasma etch cavity.

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5 The machine is governed by a programmable computer that is programmed to prompt the machine to evacuate and vent the transport chamber and plasma etching chamber, transfer wafers to and from the cassettes, elevator, and etch chamber, control the delivery of process gas, RF power, and magnetic field to the plasma etching chamber, and maintain the temperature of the wafer in the plasma etching chamber, all at appropriate times and in appropriate sequence.

10 The multilayer 10 structure is then placed within the plasma etching chamber, and etched with a fluorinated chemical etchant system to form a predetermined pattern therein. The fluorinated chemical etchant system of the present invention comprises a chemical etchant composition, such as CHF₃, CF₄, and Ar, and an additive material. The fluorinated chemical etchant system is in a substantially gaseous phase during the etching of the multilayer structure 10.

15 In the case of the chemical etchant composition including CHF₃, CF₄ and Ar, and an additive material comprising CH₂F₂, the exposed SiO₂ layer 14 is selectively etched at a relatively high etch rate and high selectivity down to the Si₃N₄ etch "stop" layer 16. Predetermined portions of the SiO₂ layer 14 are removed using chemically enhanced ionic bombardment of the gas phase etchant material.

20 An inert gas, preferably argon (Ar), is added to the etch plasma, as it tends to further enhance the uniformity of the etch process. Argon is preferred because of its weight and commercial availability, but the other inert gases can also be used.

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Heating the chamber sidewall and electrode (i.e., the wafer chuck) to higher than normal operating range, according to the present invention, produces an increase in oxide to nitride selectivity, contrary to the current teaching on high selectivity etching.

Heating the separate individual components of the chamber (e.g., sidewalls, chuck, helium backside, etc.) produced varying degrees of positive results when there was an overall increase in temperature.

Current process temperatures for highly selective etches include maintaining the etch chamber sidewalls at approximately 50°C, and the lower electrode at approximately 20°C or below, and a helium backside pressure in the approximate range of 4.0-12.0 torr.

In contrast, the preferred embodiment of the present invention involves increasing the temperature of the chamber sidewalls to a temperature in the approximate range of 50°C-100°C, and the temperature of the lower electrode is in the approximate range of 30°C-100°C, and preferably in the range of 30°C-70°C. The helium backside cooling apparatus is maintained at a pressure in the approximate range of 4.0 torr or less.

Decreasing the pressure of the helium backside cooling apparatus, essentially translates to increasing the temperature.

The reaction chamber can be heated via a fluid system, in which a fluid, such as, for example, water, at a desired temperature is flowed around the chamber walls. Alternatively, a gas can be flowed to heat the system.

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However, temperature increases in the lid or anode has produced negative results. Therefore, it is critical that the right combination of higher temperatures be maintained to produce the best selectivity. If the anode is increased to a temperature over 90°C, the photoresist layer 12 will begin to burn and reticulate. This upper temperature limitation is governed by the masking material and should not be viewed as a hard limit.

10 It is believed that increasing the temperature, also increases the rate of generation of the particular polymer species, and consequently is responsible for the increase in oxide to nitride selectivity. By increasing the temperature of the chamber, chuck, and sidewall, the selectivity is increased. Further, as the backside helium cooling was reduced, (in effect heating the wafer), the selectivity also increased.

The use of temperature control in the present invention further helps to minimize polymer build-up on the surfaces of the reaction chamber. Limiting polymer build-up substantially decreases possible contaminants, as well as downtime of the apparatus for cleaning.

25 Representative etch parameters were employed in the process for etching a multilayer structure 10 of the present invention. One having ordinary skill in the art will realize that the above values will vary depending on the make and model of the etcher used in the process.

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The flow rates of the component gases, based on the total gas flow of the fluorinated chemical etchant system, used herein was as follows: an etchant comprised of 16% CF₄, 60% Ar, 9% CH₂F₂, and 13% CHF₃, at a total pressure in the system of 225 mTorr, magnetic field maintained at 75 gauss, and RF power applied at 425 watts.

The parameters of the present invention are within the following approximate ranges: an etchant material comprised of 14 sccm CH₂F₂, 25 sccm CF₄, 90 sccm AR, and 20 sccm CHF₃, at a total pressure in the system of 225 mTorr magnetic field maintained at 75 gauss, and RF power applied at 425 watts.

Silicon dioxide and silicon nitride layers, 14 and 16 respectively, were patterned with etch masks 12 having the appropriate etch mask openings 12a and geometries. The wafers were then etched, thereby creating a substantially vertical profile in the respective films.

Figures 4a, 4b, and 4c illustrate the etch selectivities which were obtained using the process of the present invention. Figure 4a depicts the positive slope obtained on an Arrhenius plot, which slope indicates that the nitride etch rate decreases as a function of increased electrode temperature.

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All of the U.S. Patents cited herein are hereby incorporated by reference herein as if set forth in their entirety.

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While the particular process as herein shown and disclosed in detail is fully capable of obtaining the objects and advantages herein before stated, it is to be understood that it is merely illustrative of the presently preferred embodiments of the invention and that no limitations are intended to the details of construction or design herein shown other than as described in the appended claims.

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For example, one having ordinary skill in the art will realize that the present invention is also useful in etching an oxide/nitride/oxide (ONO) stack.